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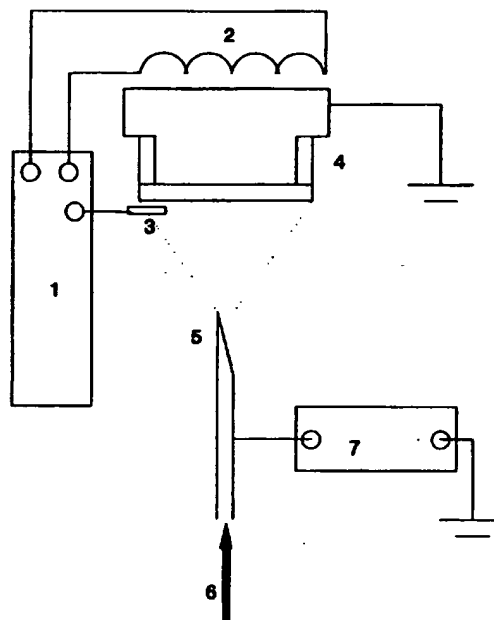
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## (54) Depositing films on a substrate using an electric field

(57) A method for the deposition of a film on a substrate, the method comprising the steps of: (a) feeding coating solution to an outlet 5 to provide a stream of droplets of said coating solution, (b) generating an electric field between said outlet and said substrate using a source 7, (c) applying a voltage to said outlet such that droplets of said coating solution emerging from said outlet are charged and attracted to said substrate by virtue of said electric field, and (d) providing an increase in temperature by heater 2 between said outlet and said substrate such that said droplets of said coating solution cluster together to form gel clusters and react with other ambient gaseous reactants in the gas phase in close proximity to said substrate thereby to form said film on said substrate. The method may be used to produce both dense and porous thin or thick films that have good adhesion to the substrate. The method may also be used for depositing films on large surface area substrates. Films produced by the method include lead zirconate titanate using the precursors  $\text{Pb}(\text{CH}_3\text{CO}_2)_2$ ,  $\text{Zr}(\text{OC}_3\text{H}_7)_4$  and  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ ;  $\text{PbTiO}_3$  using the precursors  $\text{Pb}(\text{CH}_3\text{CO}_2)_2$  and  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ ;  $\text{BaTiO}_3$  using the precursors  $\text{Ba}(\text{CH}_3\text{CO}_2)_2$  and  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ ;  $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3$ ,  $\text{La}(\text{Sr})\text{MnO}_3$ ; yttria stabilised zirconia (YSZ); or Ni-YSZ.

FIGURE 1



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FIGURE 1

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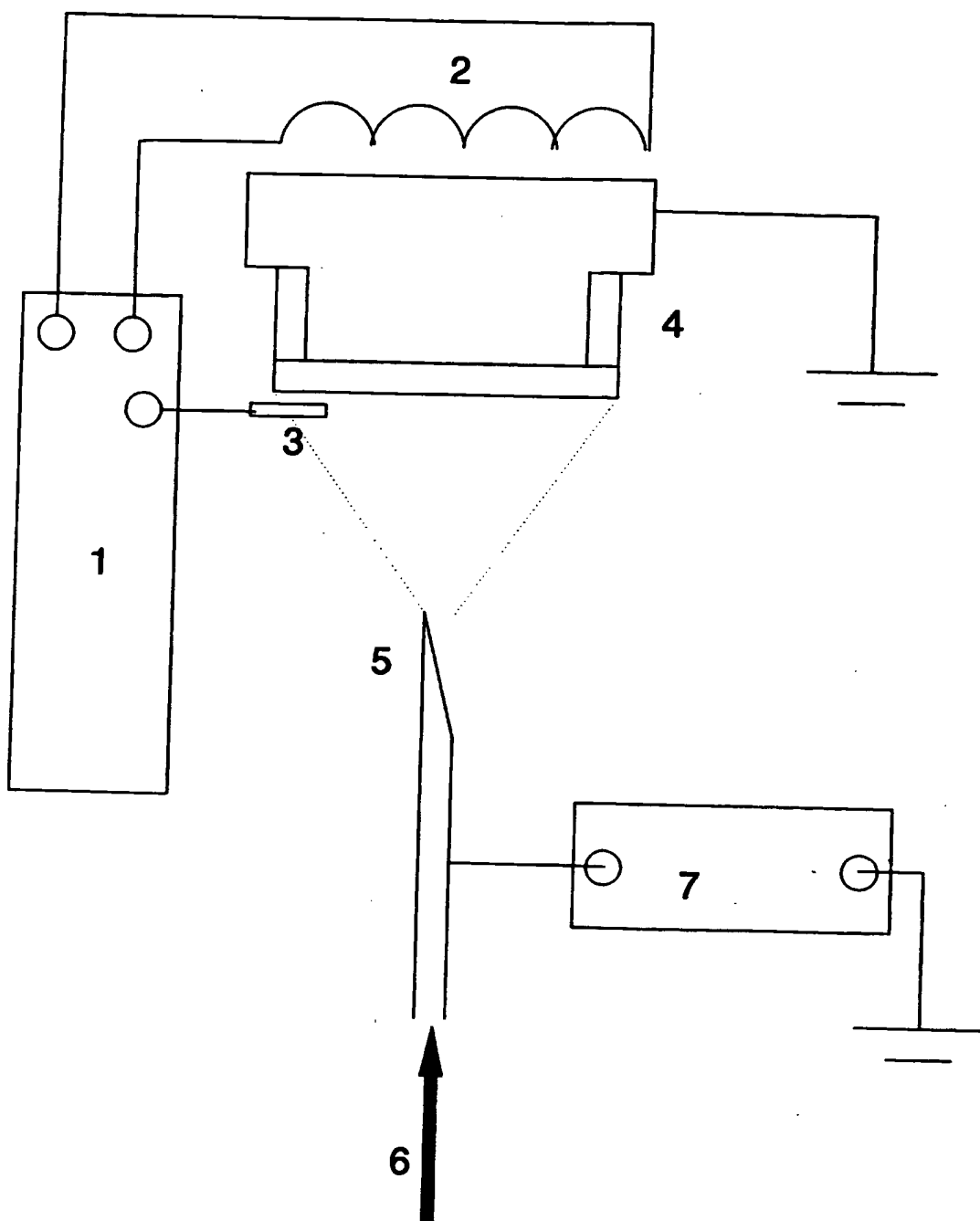


FIGURE 2

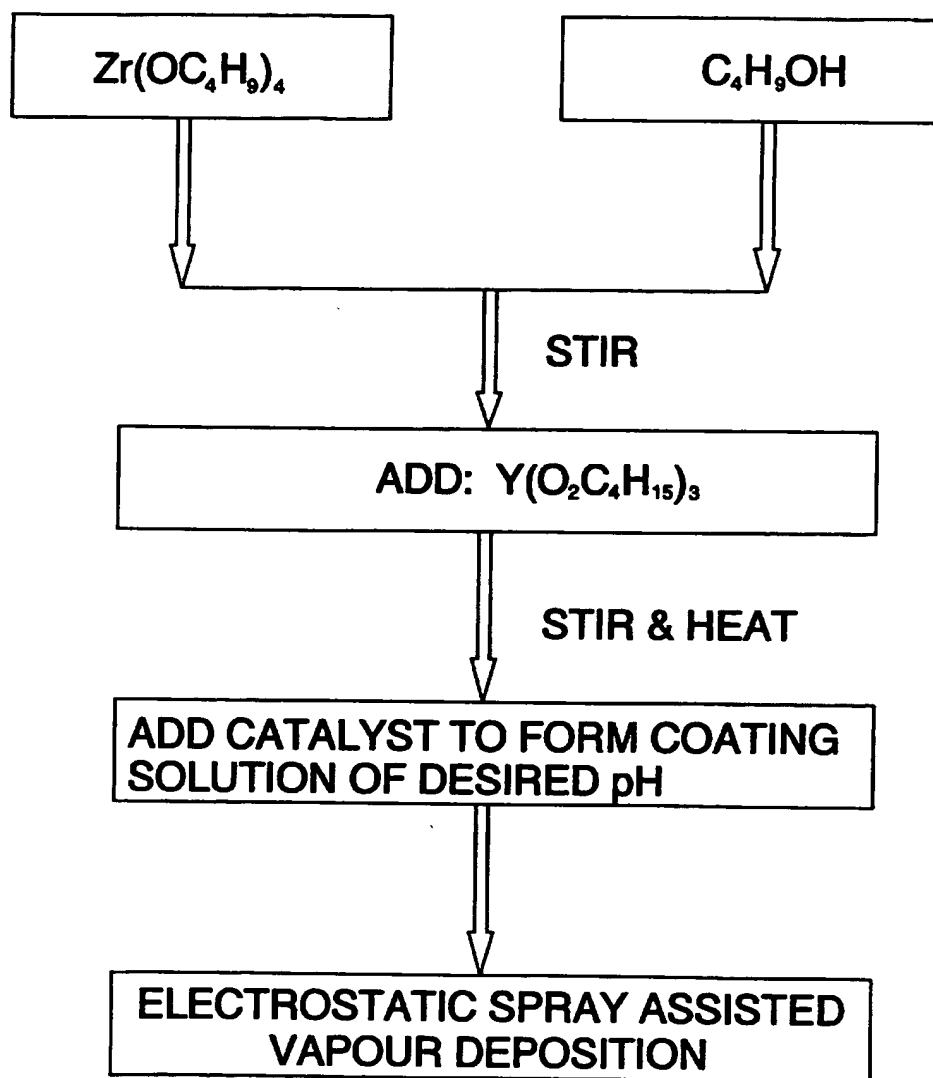
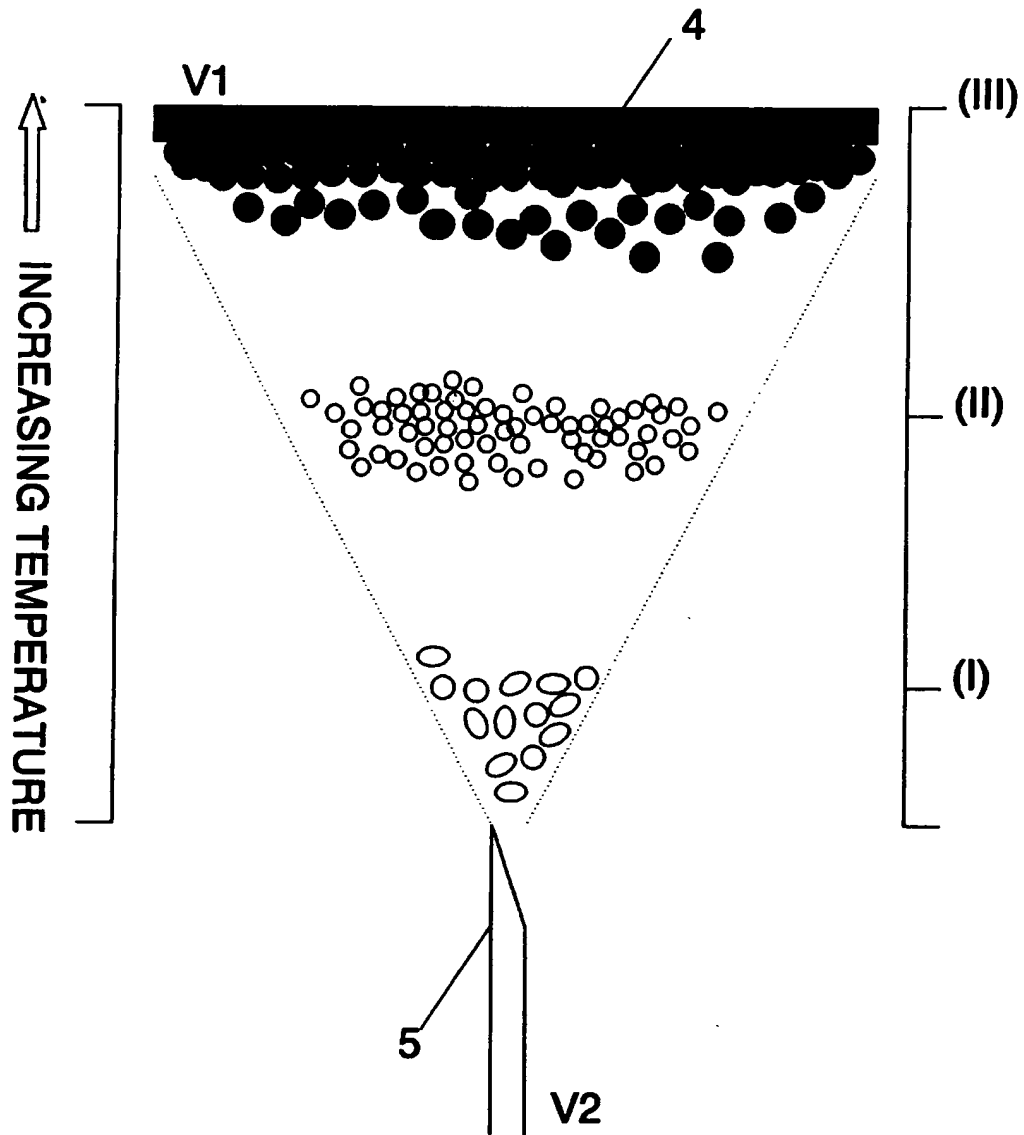


FIGURE 3



A METHOD OF DEPOSITING FILMS ON A SUBSTRATE

This invention relates to a method of depositing films on a substrate.

5 The use of ceramics in structural and functional electronic applications is widespread and expanding rapidly. For many of these increasingly demanding applications, improved materials and methods of fabrication are becoming necessary. Recently, considerable attention has been focused on the fabrication of useful films for a variety of devices. Various techniques such as chemical vapour deposition, physical vapour deposition, flame spraying deposition, and sol-gel deposition have been  
10 investigated with a view to developing a suitable method.

Chemical vapour deposition (CVD) is traditionally one of the main methods of ceramic film deposition. However, CVD often leads to difficulties in controlling the stoichiometry of multicomponent oxide films. Other problems arise from differences in the vapour pressures of CVD reagents and the relatively low growth rate of  
15 deposited film.

Physical vapour deposition (PVD) is another type of commonly used deposition process. PVD is a generic term given to a variety of sputtering techniques. Radio frequency (RF) sputtering is one of the most widely used techniques for ceramic film deposition. However, RF deposition rates are generally relatively low due to low  
20 a sputtering yield of ceramic oxide.

Reactive Magnetron Sputtering and Ion Beam Sputtering are commonly used alternative PVD techniques. Reactive Magnetron Sputtering and Ion Beam Sputtering, where a reactive background gas and an ion beam, respectively, are the primary components of the coating, allow much higher deposition rates than RF sputtering.  
25 However, all of these techniques need expensive equipment and highly skilled technicians for effective operation.

In addition to the above, the industrial application of CVD and PVD methods to ceramic films has been limited to the coating process, in which the required film thickness and coating area are relatively small. These limitations are due to the low  
30 growth rate and efficiency of the methods.

A further prior art technique, flame spray deposition (FSD), has been developed for the fabrication of multicomponent oxide ceramic thin films. This

method uses a combustion flame ( $H_2-O_2$  or  $C_2H_2-O_2$ ) to melt a spraying material and usually uses air as a carrier gas. However, it has been noted that the morphology, microstructure and electrical properties of the ceramic films formed by FSD are strongly dependent on a large number of variables. These variables include the temperature of the substrate, the coating solution concentration, the carrier gas flow rate, the coating solution flow rate, the distance between the nozzle and substrate, the atomised droplet diameter, and complex flame kinetics. In view of the complexity of the flame kinetics, the FSD process has the severe disadvantage of being extremely complex.

Other prior art methods involve the use of, so called, Sol-gel to provide a thin film. The term Sol-gel is used to describe chemical processes in which polymeric gels are formed from metallo-organic starting solutions (see for example: "Sol-gel Science" by C.Jeffrey Brinker and George W. Shearer, published in 1990). In these sol-gel processes, gel solutions are coated onto suitable substrates by spin-on, dip, or spray coating techniques, after which drying and firing stages convert the gel coating to an oxide film. However, such a sol-gel method for the production of ceramic films has two main problems associated therewith. Firstly, the films produced by these methods are easy to crack and secondly, the films have a definite thickness limit. Film cracking and the film thickness limit are major obstacles to the utilisation of sol-gel methods as a practical means of producing films of the dimensions required for many device applications.

Very recently, Electrostatic Spray Pyrolysis (ESP) or electrospraying based on the Delft Aerosol Generator (DAG) has been developed to synthesize submicron powder. This method necessitates the generation of an aerosol by the application of a high voltage potential to the nozzle. The aerosol carries with it the desired coating materials. This method has been developed in order to deposit thin films, and uses the aerosols as the absorbing species. However, the films deposited by ESP have a considerable porosity and poor adhesion. The DAG is an article of laboratory equipment based upon the principle of the Taylor Cone and was named by G.M.H.Meesters et al in "Generation of Micron-Sized Droplets from the Taylor Cone" - Journal of Aerosol Science, Volume 23, No. 1, pp 37-42, published in 1992.

In accordance with the present invention, there is provided a method for the

deposition of a film on a substrate, the method comprising the steps of:

- (a) feeding coating solution to an outlet to provide a stream of droplets of said coating solution,
- (b) generating an electric field between said outlet and said substrate,
- 5 (c) applying a voltage to said outlet such that droplets of said coating solution emerging from said outlet are charged and attracted to said substrate by virtue of said electric field, and
- 10 (d) providing an increase in temperature between said outlet and said substrate such that said droplets of said coating solution cluster together to form gel clusters and react with other ambient gaseous reactants in the gas phase in close proximity to said substrate thereby to form said film on said substrate.

Embodiments of this method, which will be referred to hereinafter as electrostatic spray assisted vapour deposition (ESAVD), enable the fabrication of both  
15 thin and thick films. The technique combines the advantages of CVD and electrostatic spray deposition whilst alleviating the problems associated therewith. In comparison to other film deposition techniques, ESAVD has a high deposition rate and efficiency, and allows easy control of the stoichiometry and microstructure of the deposits. In addition, it is a simple, cheap, and low-temperature synthesis method suitable for the  
20 fabrication of a variety of different films. The method also allows the deposition of a film on large surface area substrates.

With reference to the above, it should be understood that as the present method is intended, in one embodiment, to be performed in such a fashion that the substrate and other pieces of apparatus are open to the surrounding ambient atmosphere, the  
25 other ambient gaseous reactants refer to any other gaseous reactants (such as Oxygen, for example) that may be present in the atmosphere. In another embodiment, the present method may performed within the confines of a container and said other ambient gaseous reactants may be supplied to said container, thereby to enable the deposition of a particular film.

30 Both simple and multicomponent ceramic oxide films have been fabricated using the above mentioned method. In one embodiment, the film may be a ceramic film such as PZT (Lead Zirconate Titanate) or a doped film such as YSZ (Yttria



Stabilised Zirconia). Other films may include  $\text{PbTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{La}(\text{Sr})\text{MnO}_3$ , Ni-YSZ,  $\text{SnO}_2$ - $\text{In}_2\text{O}_3$  and other Indium-Tin Oxide films. The film may also be a structural and/or functional film such as an electroceramic film.

Preferably, the droplets are charged to approximately 30 kilovolts with respect to the substrate.

In one aspect, the temperature increases from about 100 to about 600 degrees celsius. In another aspect, the temperature increases from about 100 to about 400 degrees celsius. Varying the processing parameters enables the production of dense/porous and/or thin/thick films all of which have good adhesion to the substrate.

Preferably, the film has a thickness between a nanometre and approximately 100 micrometers.

As mentioned above, the film may be Lead Zirconate Titanate (PZT). In which case, the coating solution may be manufactured by the steps of:

- (a) mixing  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$  (solvent) with a first precursor compound  $\text{Pb}(\text{CH}_3\text{CO}_2)_2$  and  $\text{Zr}(\text{OC}_3\text{H}_7)_4$  and a second precursor compound  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , and
- (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

Alternatively, the film may be  $\text{PbTiO}_3$ . In which case, the coating solution may be manufactured by the steps of:

- (a) mixing  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$  (solvent) with a first precursor compound  $\text{Pb}(\text{CH}_3\text{CO}_2)_2$  and a second precursor compound  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , and
- (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

Alternatively, the film may be  $\text{BaTiO}_3$ . In which case, the coating solution may be manufactured by the steps of:

- (a) mixing  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$  (solvent) with a first precursor compound  $\text{Ba}(\text{CH}_3\text{CO}_2)_2$  and a second precursor compound  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , and
- (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

Alternatively, the film may be  $\text{SnO}_2$ - $\text{In}_2\text{O}_3$ . In which case, the coating solution may be manufactured by the steps of:

- (a) mixing ethanol (solvent) with a first precursor compound  $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  and a second precursor compound  $\text{SnCl}_2$ , and
- (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

5 Alternatively, the film may be  $\text{La}(\text{Sr})\text{MnO}_3$ . In which case, the coating solution may be manufactured by the steps of:

- (a) mixing about 20%  $\text{H}_2\text{O}$  and about 80% ethanol (solvent) with a first precursor compound  $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  and  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a second precursor compound  $\text{SrNO}_3$ , and
- 10 (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

Alternatively, the film may be Yttria Stabilised Zirconia (YSZ). In which case, the coating solution may be manufactured by the steps of:

- 15 (a) mixing propanol or butanol (solvent) with a first precursor compound  $\text{Y}(\text{O}_2\text{C}_8\text{H}_{15})_3$  and a second precursor compound  $\text{Zr}(\text{OC}_4\text{H}_9)_4$ , and
- (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

or, in a second aspect, by the steps of:

- 20 (a) mixing propanol or butanol (solvent) with a first precursor compound  $\text{Y}(\text{O}_2\text{C}_8\text{H}_{15})_3$  and a second precursor compound  $\text{Zr}(\text{OC}_3\text{H}_7)_4$ , and
- (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

Alternatively, the film may be Ni-YSZ. In which case, the coating solution may be manufactured by the steps of:

- 25 (a) mixing propanol (solvent) with a first precursor compound  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Zr}(\text{OC}_3\text{H}_7)_4$  and a second precursor compound  $\text{Y}(\text{O}_2\text{C}_8\text{H}_{15})_3$ , and
- (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

30 In any of the above aspects, the catalyst may be an acid such as ethanoic acid or hydrochloric acid. In which case, the required pH may be between 2 and 5.

Alternatively, the catalyst may be an alkali such as  $\text{NH}_3$ . In which case, the

required pH may be between 9 and 12.

In accordance with the present invention, there is also provided an apparatus for depositing films on a substrate, comprising:

- (a) an outlet for providing a stream of coating solution droplets,
- 5 (b) a voltage source for applying a charge to said outlet and said coating solution droplets flowing therethrough,
- (c) generating means for generating an electric field between said outlet and said substrate, said field serving to guide said charged droplets to said substrate,
- 10 (d) a heater for heating said substrate and providing an increase in temperature between said outlet and said substrate.

The heater may be controlled by a controller, said controller being connected to a temperature sensor for providing said controller with temperature information.

The apparatus may further comprise a syringe pump or a static pressure feed  
15 to provide a constant stream of coating solution to said outlet.

The apparatus may also comprise a container capable of enclosing at least said substrate and said outlet, such that other gaseous reactants may be supplied for reaction with said coating solution.

The present invention will now be described, by way of example only, with  
20 reference to the appended drawings in which:

Figure 1 illustrates schematically an apparatus for use in electrostatic spray assisted vapour deposition of a film on a substrate;

Figure 2 is a flow chart that illustrates schematically steps in the synthesis of coating solution for the electrostatic spray assisted vapour deposition of YSZ; and

25 Figure 3 schematically illustrates the principle of electrostatic spray assisted vapour deposition of a film from a coating solution using the apparatus of Figure 1.

The present embodiment utilises a coating solution to form a ceramic film on a substrate.

One example of an apparatus for use in film deposition is shown in Figure 1.  
30 The present method utilises a high electrostatic potential field and a discharge outlet 5. In one embodiment, the outlet may be a nozzle. The outlet 5 is connected to a high voltage DC source 7 preferably variable in the range 0-30 kV. A substrate holder

4 is earthed and provided in the proximity of the outlet 5. The substrate holder 4 is heated by the heater 2, the temperature being controlled by the controller 1 and an attached thermocouple 3. Heating of the substrate causes a corresponding heating of the area surrounding the substrate 4 and in front of the outlet 5. This heating serves to set up a temperature gradient whereby the ambient temperature increases as the substrate is approached from the direction of the outlet. This increased temperature facilitates a chemical vapour reaction of the coating solution that enables deposition of the ceramic film. This reaction is further described below in relation to Figure 3. When an electric field of sufficient strength is applied to the outlet 5, a corona field is produced from the tip of the outlet 5. A ceramic coating liquid is used to form the films and is fed into the outlet 5 in the direction indicated by arrow 6. The outlet's inner diameter can vary from 1mm (millimeter) to 0.1mm. This relatively large inner diameter ensures that the likelihood of clogging problems with high viscosity solutions in the outlet 5 is significantly reduced.

In one embodiment, a constant flow is maintained by use of a syringe pump or a constant static pressure feed. Preferably, the solution flow is in the range of 0.4 - 10 ml/h (millilitres per hour).

In this way, the electrostatic field set up between the charged outlet 5 and the earthed substrate holder 4 serves to guide charged coating solution droplets to the substrate 4. Droplets of the coating solution are provided with a positive charge by way of the high voltage DC source 7. These positively charged droplets are attracted to the earthed substrate holder 4. As an alternative, the droplets could be negatively charged with an earthed holder 4, or vice versa.

One embodiment of coating solution synthesis procedures is illustrated in Figure 2. Alternative methods involve coating solution synthesis of YSZ or Organometallic compound synthesis (including metal alkoxide synthesis).

With reference to Figure 2, the preparation of one type of coating solution for the deposition of YSZ (Yttria Stabilised Zirconia) is shown. As a first step, a precursor compound (in this case,  $Zr(OC_4H_9)_4$ ) is mixed with a solvent (in this case, Butanol -  $C_4H_9OH$ ). This solution is stirred and a second precursor compound, usually a metal alkoxide (in this case,  $Y(O_2C_4H_9)_3$ ) or organometallic compound is added under action of heat. The mixture is then catalysed to form a coating solution of the

desired pH. In this case, ethanoic acid ( $\text{CH}_3\text{COOH}$ ) is used as a catalyst, but other acids (such as HCL) or alkalis (such as  $\text{NH}_3$ ) may be used in the preparation of alternative coating solutions. In the case of acid catalysed reactions, the desired pH may be between 2 and 5. In the case of alkali catalysed reactions, the desired pH may be between 9 and 12.

The coating solution, which is in this case is a mixture of  $\text{Zr}(\text{OC}_4\text{H}_9)_4$ , Butanol, Water and  $\text{Y}(\text{O}_2\text{C}_4\text{H}_9)_3$ , is then passed to the outlet 5 and discharged towards the substrate 4.

Preferably, the concentration of the desired coating solution is approximately 0.01-0.1 mol/l (moles per litre). In addition, the coating solution may have a viscosity in the region of about 5 to 50 mPa.S (millipascal seconds) depending on the type of film that it is desired to produce.

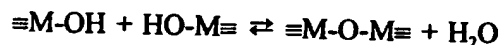
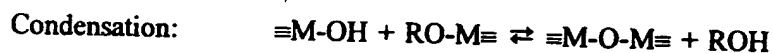
As mentioned above, a variety of different films may be deposited by the present method. Given below is a table showing the constituent compounds used to manufacture a suitable coating solution for each desired deposited film.

| Film                                 | 1st Precursor   | 2nd Precursor                        | Solvent  | Catalyst      |
|--------------------------------------|---|--------------------------------------|--|---------------|
| PZT                                  | $\text{Pb}(\text{CH}_3\text{CO}_2)_2$<br>& $\text{Zr}(\text{OC}_3\text{H}_7)_4$                                   | $\text{Ti}(\text{OC}_3\text{H}_7)_4$ | $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$        | Ethanoic Acid |
| $\text{PbTiO}_3$                     | $\text{Pb}(\text{CH}_3\text{CO}_2)_2$   | $\text{Ti}(\text{OC}_3\text{H}_7)_4$ | $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$        | Ethanoic Acid |
| $\text{BaTiO}_3$                     | $\text{Ba}(\text{CH}_3\text{CO}_2)_2$   | $\text{Ti}(\text{OC}_3\text{H}_7)_4$ | $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$        | Ethanoic Acid |
| $\text{SnO}_2\text{-In}_2\text{O}_3$ | $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  | $\text{SnCl}_2$                      | Ethanol  | Ethanoic Acid |
| $\text{La}(\text{Sr})\text{MnO}_3$   | $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$<br>&<br>$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | $\text{SrNO}_3$                      | 20% $\text{H}_2\text{O}$ and<br>about 80%<br>ethanol | Ethanoic Acid |

| Film   | 1st Precursor                                 | 2nd Precursor       | Solvent             | Catalyst      |
|--------|---|---------------------|---------------------|---------------|
| YSZ    | $Y(O_2C_8H_{15})_3$                           | $Zr(OC_4H_9)_4$     | Propanol or Butanol | Ethanoic Acid |
| YSZ    | $Y(O_2C_8H_{15})_3$                           | $Zr(OC_3H_7)_4$     | Propanol or Butanol | Ethanoic Acid |
| Ni-YSZ | $Ni(NO_3)_2 \cdot 6H_2O$<br>& $Zr(OC_3H_7)_4$ | $Y(O_2C_8H_{15})_3$ | Propanol            | Ethanoic Acid |

Whilst the table above shows Ethanoic Acid as the desired catalyst, it will be remembered that alternative acids and/or alkalis may be used instead.

Figure 3 illustrates the principle of electrostatic spray assisted vapour deposition of a film from a coating solution. The temperature gradient preferably increases from about 100°C to between 400 and 600°C. At point (I) on Figure 3, the coating solution forms a corona spray, the droplets of which are charged to a positive potential. As the droplets are attracted to the substrate 4 they begin to cluster together (shown at point (II) in Figure 3) to form a gel under the influence of an increased ambient temperature. At point (III) in Figure 3, the gel and/or clusters decompose and/or react in close proximity to the substrate to form the desired ceramic film. The gel may also react with other gaseous reactants such as Oxygen. The hydrolysis/condensation reaction for the production of a Sol→gel transition is as follows:



Where M is the desired metal film element (in this case, Zirconium) and R is  $C_4H_9$ . In this method, the chemical reaction proceeds forwards (towards the right hand side of the above equations) and the reaction time decreases, with increasing temperature. Thus, the hydrolysis/condensation reaction is speeded up with increasing temperature.

With reference to the above, it will be understood that as the present method

is intended, in one embodiment, to be operated in such a fashion that the substrate and other pieces of apparatus are open to the surrounding ambient atmosphere, the other ambient gaseous reactants refer to any other gaseous reactants (such as Oxygen, for example) that may be found in the atmosphere. In another embodiment, the present method may performed within the confines of a container, and any desired ambient gaseous reactants (such as hydrogen sulphide, for example) may be introduced into that container. These introduced gases may react with the gel to form particular films (such as sulphide or nitrite films, for example) on the substrate.

To summarise, during ESAVD, droplets of coating solution are charged and then transform into clusters or fine particles of gel between the discharge outlet 5 and the substrate 4. This transformation occurs under the action of a corona field and an elevated temperature. These clusters and fine droplets of gel are then attracted to the substrate by virtue of the induced electric field. The temperature gradient is such that the gel and other gaseous reactants coexist around the substrate 4. The particles or clusters of gel undergo decomposition and/or chemical reaction with gaseous reactants just on or in very close proximity to the substrate surface 4. Chemical reactions involving coating solution gel cause the formation of the desired ceramic film - as illustrated in Figure 3.

As this method operates on a principle whereby charged droplets from the outlet 5 are attracted towards a grounded substrate, it is particularly suitable for scanning or writing large surface areas and is not restricted to particular chamber sizes as in CVD and PVD. Growth rates achievable with this method were found to be between 0.1 and 5 microns per minute depending upon the concentration and flow rate of coating solution.

The achievable microstructure, grain size, particle distribution, surface morphology and thickness of ceramic film are strongly dependant on the process conditions. The grain size in the deposited film is mainly determined by the droplet size, and the flow rate, viscosity and concentration of coating solution. For example, the grain size of ceramic films increases and uniformity of the grain distribution decreases as the droplet sizes, flow rates, concentration and viscosity of coating solution increase. Similarly, droplet sizes are mainly determined by the corona field intensity and coating liquid conductivity. The mean droplet size decreases with

increasing coating liquid conductivity. Thus, films with nanosize grained microstructure can be deposited with the ESAVD technique.

The crystal phase structures of the ceramic films deposited by the present technique are mainly determined by the temperature of the substrate 4. Ceramic films formed at lower substrate temperatures, have an amorphous or nanocrystalline crystal phase. These films may then be treated by an additional sintering process, to transform the crystal structure from an amorphous or nanocrystalline structure to the desired ceramic phase. A higher substrate temperature during deposition results in an increase in crystallinity of the ceramic film deposited thereupon.

It will be understood, of course, that the above method is not to be limited to the deposition of any particular ceramic films. Indeed, various kinds of film, such as simple oxide films, multicomponent oxide films (e.g. PZT (Lead Zirconate Titanate -  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ),  $\text{PbTiO}_3$ ,  $\text{BaTiO}_3$ , Indium Tin Oxide or  $\text{La}(\text{Sr})\text{MnO}_3$ ) or doped films (e.g. YSZ (Yttria Stabilised Zirconia -  $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$ ) or Ni-YSZ) etc may be produced with this technique. The present method may also be used to produce films other than ceramics. The present method may also be used to deposit structural and/or functional films such as electroceramic films, or to deposit nanostructured films.

Similarly, the method described above is not limited to the production of thick or thin films. Indeed, it has been found that the present invention may be used to produce films of a thickness varying from a nanometre to approximately 100 micrometers in thickness.

In addition, it will be appreciated that the outlet referred to herein encompasses any sort of outlet including a nozzle, a spray or other similar apparatus.



CLAIMS

1. A method for the deposition of a film on a substrate, the method comprising the steps of:

- 5           (a) feeding coating solution to an outlet to provide a stream of droplets of said coating solution,
- (b) generating an electric field between said outlet and said substrate,
- (c) applying a voltage to said outlet such that droplets of said coating solution emerging from said outlet are charged and attracted to said
- 10           substrate by virtue of said electric field, and
- (d) providing an increase in temperature between said outlet and said substrate such that said droplets of said coating solution cluster together to form gel clusters and react with other ambient gaseous reactants in the gas phase in close proximity to said substrate thereby to form said
- 15           film on said substrate.

2. A method according to Claim 1 wherein said film is a ceramic film.

3. A method according to Claim 1 or Claim 2 wherein said film is a

20           multicomponent oxide film.

4. A method according to any one of Claims 1 to 3 wherein said film is Lead Zirconate Titanate (PZT).

25           5. A method according to Claim 4 wherein said coating solution is manufactured by the steps of:

- (a) mixing  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$  (solvent) with a first precursor compound  $\text{Pb}(\text{CH}_3\text{CO}_2)_2$  and  $\text{Zr}(\text{OC}_3\text{H}_7)_4$  and a second precursor compound  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , and
- 30           (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

6. A method according to any one of Claims 1 to 3 wherein said film is  $\text{PbTiO}_3$ .

7. A method according to Claim 6 wherein said coating solution is manufactured by the steps of:

- 5
- (a) mixing  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$  (solvent) with a first precursor compound  $\text{Pb}(\text{CH}_3\text{CO}_2)_2$  and a second precursor compound  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , and
  - (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

10 8. A method according to any one of Claims 1 to 3 wherein said film is  $\text{BaTiO}_3$ .

9. A method according to Claim 8 wherein said coating solution is manufactured by the steps of:

- 15
- (a) mixing  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$  (solvent) with a first precursor compound  $\text{Ba}(\text{CH}_3\text{CO}_2)_2$  and a second precursor compound  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , and
  - (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

20 10. A method according to any one of Claims 1 to 3 wherein said film is  $\text{SnO}_2$ - $\text{In}_2\text{O}_3$ .

11. A method according to Claim 10 wherein said coating solution is manufactured by the steps of:

- 25
- (a) mixing ethanol (solvent) with a first precursor compound  $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  and a second precursor compound  $\text{SnCl}_2$ , and
  - (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

30 12. A method according to any one of Claims 1 to 3 wherein said film is  $\text{La}(\text{Sr})\text{MnO}_3$ .

13. A method according to Claim 12 wherein said coating solution is manufactured by the steps of:
- (a) mixing about 20%  $\text{H}_2\text{O}$  and about 80% ethanol (solvent) with a first precursor compound  $\text{La}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  and  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a second precursor compound  $\text{SrNO}_3$ , and
  - (b) adding a catalyst to said mixture to provide a coating solution of a required pH.
14. A method according to Claim 1 or Claim 2 wherein said film is a simple oxide film.
15. A method according to Claim 1 or Claim 2 wherein said film is a doped film.
16. A method according to Claim 15 wherein said film is Ytria Stabilised Zirconia (YSZ).
17. A method according to Claim 16 wherein said coating solution is manufactured by the steps of:
- (a) mixing propanol or butanol (solvent) with a first precursor compound  $\text{Y}(\text{O}_2\text{C}_8\text{H}_{15})_3$  and a second precursor compound  $\text{Zr}(\text{OC}_4\text{H}_9)_4$ , and
  - (b) adding a catalyst to said mixture to provide a coating solution of a required pH.
18. A method according to Claim 16 wherein said coating solution is manufactured by the steps of:
- (a) mixing propanol or butanol (solvent) with a first precursor compound  $\text{Y}(\text{O}_2\text{C}_8\text{H}_{15})_3$  and a second precursor compound  $\text{Zr}(\text{OC}_3\text{H}_7)_4$ , and
  - (b) adding a catalyst to said mixture to provide a coating solution of a required pH.
19. A method according to Claim 15 wherein said film is Ni-YSZ.

20. A method according to Claim 19 wherein said coating solution is manufactured by the steps of:

- (a) mixing propanol (solvent) with a first precursor compound  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Zr}(\text{OC}_3\text{H}_7)_4$  and a second precursor compound  $\text{Y}(\text{O}_2\text{C}_8\text{H}_{15})_3$ , and
- (b) adding a catalyst to said mixture to provide a coating solution of a required pH.

21. A method according to any one of Claims 1 to 20 wherein said film is a structural film.

22. A method according to any one of Claims 1 to 21 wherein said film is a functional film.

23. A method according to Claim 21 or Claim 22 wherein said film is an electroceramic film.

24. A method according to any one of Claims 5, 7, 9, 11, 13, 17 or 20 wherein said catalyst is an acid.

25. A method according to Claim 24 wherein said catalyst is ethanoic acid.

26. A method according to Claim 24 wherein said catalyst is hydrochloric acid.

27. A method according to Claim 25 or Claim 26 wherein said required pH is between 2 and 5.

28. A method according to any one of Claims 5, 7, 9, 11, 13, 17 or 20 wherein said catalyst is an alkali.

29. A method according to Claim 28 wherein said catalyst is  $\text{NH}_3$ .

30. A method according to Claim 28 or Claim 29 wherein said required pH is between 9 and 12.

31. A method according to any one of Claims 1 to 30 wherein said droplets of coating solution are charged to approximately 30 kilovolts with respect to the substrate.

32. A method according to any one of Claims 1 to 31 wherein said temperature increases from about 100 to about 600 degrees celsius.

33. A method according to any one of Claims 1 to 32 wherein said temperature increases from about 100 to about 400 degrees celsius.

34. A method according to any one of Claims 1 to 33 wherein said film has a thickness between a nanometre and approximately 100 micrometers.

35. A method according to any one of Claims 1 to 34 wherein said method is performed within the confines of a container and said other ambient gaseous reactants are supplied to said container, thereby to enable the deposition of a particular film.

36. Apparatus for depositing films on a substrate, comprising:

- (a) an outlet for providing a stream of coating solution droplets,
- (b) a voltage source for applying a charge to said outlet and said coating solution droplets flowing therethrough,
- (c) means for generating an electric field between said outlet and said substrate, said field serving to guide said charged droplets to said substrate,
- (d) a heater for heating said substrate and providing an increase in temperature between said outlet and said substrate

37. An apparatus according to Claim 36 wherein said heater is controlled by a controller, said controller being connected to a temperature sensor for providing said

controller with temperature information.

38. An apparatus according to Claim 36 or Claim 37 further comprising a syringe pump to provide a constant stream of coating solution to said outlet.

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39. An apparatus according to Claim 36 or Claim 37 further comprising a static pressure feed to provide a constant stream of coating solution to said outlet.

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40. An apparatus according to any one of Claims 36 to 39 further comprising a container capable of enclosing at least said substrate and said outlet, such that other gaseous reactants may be supplied for reaction with said coating solution.

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41. A method of depositing a film on a large area substrate by operating the apparatus according to claim 36 in accordance with the method according to any one of Claims 1 to 35.

42. A method substantially as hereinbefore described with reference to the accompanying drawings.

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43. An apparatus substantially as hereinbefore described with reference to the accompanying drawings.



Application N : GB 9525505.5  
Claims searched: 1-43

Examiner: Peter Beddoe  
Date of search: 22 April 1996

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK CI (Ed.O): C7F (FHB,FHD,FHE,FHX)  
Int CI (Ed.6): C23C (16/40,16/44,16/50,18/12); H01L 39/24, C03C 17/25; C04B 41/50  
Other: Online: WPI, CLAIMS

**Documents considered to be relevant:**

| Category | Identity of document and relevant passage                          | Relevant to claims |
|----------|--|--------------------|
| Y        | GB 2282825 A (MITSUBISHI) see esp p. 13 l. 10 - P. 14 l. 4         | 1,36               |
| Y        | GB 2258247 A (KABUSHIKI) see esp p. 8 l. 12 - P. 9 l. 18           | 1,36               |
| X        | GB 2192901 A (UNVALA) see esp p. 2 l. 41 - p. 3 l. 35, Fig 1       | 1,36               |
| X        | GB 1291192 A (RANSBURG) see esp example                            | 1,36               |
| X        | GB 1202573 A (WESTERN) see esp example 1                           | 1,36               |
| X        | EP 0183254 A2 (MATSUSHITA) see esp p. 15 l. 4 - p. 16 l. 22; Fig 1 | 1,36               |
| X        | EP 0066288 A1 (TOKYO) see esp p. 8 l. 15 - p. 9 l. 22              | 1,36               |
| X        | US 5399388 (AKLUFU) see esp col. 4-6, Fig 1                        | 1,2,36             |
| X        | US 3436257 (MYERS) see esp col. 4 l. 43 - 57, example 1            | 1,36               |

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|---|---|---|--|
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